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The crystal structure of μ-Oxo-bis{diethoxy[salicylaldoximato(2-)]-tantalum(V)}

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ABSTRACT

Stochiometric reaction of salicylaldoxime and tantalum or niobium ethoxide in toluene at room temperature resulted in formation of $[M_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$, M=Ta and Nb which were crystallized from CH_2Cl_2 at −5 °C and characterized by spectroscopic techniques. The molecular structures of $[Ta_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ was determined by single-crystal X-ray diffraction and compared with molecular structure of $[Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$. The geometries at metal atoms are distorted octahedron which shared an apex through bridged oxygen. Each dianionic salicylaldoximate ligand chelates to the one metal ion through its phenolic oxygen and oximate nitrogen atoms, and to another metal ion through its oximate oxygen atom.

1. Introduction

Metal oxo-bridged alkoxides are important intermediates of oligomeric metal alkoxides and metal oxides and they can be products of controlled hydrolysis of metal alkoxide or side product in preparation of metal alkoxides from metal oxide. They are also produced by ether elimination from metal alkoxides or reaction of metal oxo-chlorides with alkali alkoxides [1]. Although their hydrolytic stability increases with oxo content [2], they are still reactive toward water or alcohol exchange processes and stabilizing them with chelating ligands is subject of interest and desire in sol-gel processing. Numbers of chelating ligands have been used for the stabilization of metal oxo-bridged alkoxides, such as polyols [3], carboxylates [4,5], β-diketonates [6] and alkanolamines [7] and a variety of their derivatives have been isolated. Interestingly, the stabilized metal alkoxides show different behavior in the hydrolysis-condensation process and that reflects in the properties of final materials [8]. This approach has been used in industry for tailoring metal oxides with well-defined specification for the fabrication of advanced ceramics. Evidently, the stability of modified metal oxo-alkoxides depends on the type of ligands and coordination status of them. Apparently, hydrolytic stability of metal alkoxides increases by decreasing the number of alkoxy groups, and consequently their alkoxy character vanishes, in which their hydrolysis requires harsh media [2]. Recent studies show that, due to the lability of metal oxo-alkoxides, alkoxy groups quite readily can be replaced by a wide variety of ligands containing hydroxyl group [9–11]. Over the last decade, several efforts have been conducted to elucidation of coordination chemistry of salicylaldoxime and its derivatives due to the ability of the dianions of those ligands to produce high nuclearity metal complexes [12]. Salicylaldoxime (2-hydroxybenzaldehyde oxime), which is a primitive member of phenolic oxime ligands, has been mentioned in a 1964 edition of Vogel's textbook of inorganic analysis as an inorganic reagent. This ligand chelates to metal ion through the phenolic oxygen and oximate nitrogen atoms in mono-deprotonated form. Interestingly, the free OH oxime group of complex usually

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engages in hydrogen bonding with water molecules or phenolic oxygen atoms of neighboring salicylaldoxime ligands [13,14] or other molecules [15] to stabilize structure. In the mono-deprotonated form, 2-hydroxybenzaldehydeoxime usually produces mono- or bi-nuclear complexes, which are used in separation analysis, metal extraction and nano-crystal preparation [16]. In a doubly-deprotonated anion, salicylaldoxime usually uses its phenolic oxygen and oximate nitrogen atoms to chelate to one metal ion and its oximate oxygen as bridging unit to bonds to neighboring metal ion, so it can produce poly-nuclear complexes in this form. These poly-nuclear complexes are relevant to several areas of science and technology, including corrosion inhibition [17]. To the best of our knowledge, there is a limited number of structurally characterized doubly-deprotonated salicylaldoxime of alkoxide complexes [10,18,19] and this is the first report on tantalum alkoxide complexes with salicylaldoxime. During the course of stabilization of metal alkoxides for the fabrication of metal oxides and in the interest in how structural modification would alter the final texture of metal oxides, we have prepared salicylaldoxime derivatives of tantalum and niobium alkoxides. Herein, we report synthesis and characterization of two dinuclear complexes of Ta(V) and Nb(V) with salicylaldoxime, $[M_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$, M=Ta (**I**) and Nb (**II**). These complexes were characterized by ^1H, ^{93}Nb-NMR, UV-Vis and Mass spectrometry, in addition to the single-crystal structure of **II** in light of our pervious study [9].

2. Materials and methods

All manipulations were carried out under nitrogen, using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Salicylaldoxime [20], niobium(V) pentaethoxide and tantalum(V) pentaethoxide [1] were prepared according to the reported procedures. IR spectra were recorded on a Shimadzo 470 instrument at 4 cm^{-1} resolution, using KBr pellets. The ^1H and ^{93}Nb-NMR spectra were obtained in $CDCl_3$ using a Brucker DRX-500 spectrometer. The mass spectrometery was performed on a Varian Matt 44 instrument (electron impact, 20 eV). UV-Vis spectra were recorded on a Shimadzo 2100 spectrophotometer.

3. Experimental

3.1. Preparation of metaloorganic compounds

3.1.1. $[Ta_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ (I)

Compound **I** was prepared by reaction of salicylaldoxime (0.55 g, 4 mmol) with $Ta(OCH_2CH_3)_5$ (1.62 g, 4mmol) in toluene (10 mL). The mixture was stirred for a day and the solvent then was removed under reduced pressure to furnish a yellowish solid. The solid was crystallized from dichloromethane-ether. Suitable crystals of complex for single-crystal structure determination were isolated from solution after several days at −5 °C (m.p., decomposed at 270 °C). Anal. Calcd. for $C_{22}H_{30}N_2O_9Ta_2$: C, 31.88; H, 3.62; N, 3.38%. Found: C, 32.06; H, 3.84; N, 3.23%. UV (CH_2Cl_2, nm): 246 (LMCT), 280 (π to π^*), 345 (n to π^*). IR (cm^{-1}): 3058 (C-H, aromatic), 2920 (C-H, aliphatic), 1600 (C=N), 1556 (C=C), 1287 (C-O), 670 (Ta-O-C, symmetric), 577 (Ta-O-C, asymmetric). ^1H-NMR ($CDCl_3$, ppm): 1.02 (6H, t, CH_3), 1.46 (6H, t, -CH_3), 4.21 (4H, q, -OCH_2-), 4.81 (4H, q, -OCH_2-), $C_7H_5NO_2$ ligand protons: 6.90 (4H, m), 7.12 (2H, m), 7.37 (2H, m), 8.14 (2H, s, CH=N).

3.1.2. $[Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$ (II)

Compound **II** was prepared, according to the earlier report [9], by reacting salicylaldoxime (0.55 g, 4 mmol) to $Nb(OCH_2CH_3)_5$ (1.27 g, 4 mmol) in toluene (10 mL). The mixture was stirred for a day and the solvent then was removed under reduced pressure to furnish an orange solid. The solid was crystallized from dichloromethane/hexane; crystals of complex were isolated from solution after several days at −5 °C. (m.p., decomposed at 250 °C). Anal. Calcd. for $C_{22}H_{30}N_2O_9Nb_2$: C, 40.49; H, 4.60; N, 4.29%. Found: C, 40.86; H, 4.72; N, 4.16%. UV (CH_2Cl_2, nm): 231 (LMCT), 277 (π to π^*), 357 (n to π^*). IR (cm^{-1}): 3045 (C-H, aromatic), 2905 (C-H, aliphatic), 1592 (C=N), 1553 (C=C), 1278 (C-O), 671 (Nb-O-C, symmetric), 579 (Nb-O-C, asymmetric). ^1H-NMR ($CDCl_3$, ppm): 1.16 (6H, t, CH_3), 1.45 (6H, t, -CH_3), 4.47 (4H, q, -OCH_2-), 4.62 (4H, q, -OCH_2-), $C_7H_5NO_2$ ligand protons: 6.88 (4H, m), 7.09 (2H, dd), 7.30 (2H, dt), 7.94 (2H, s, CH=N). ^{93}Nb-NMR ($CDCl_3$, ppm): 132 (6 coordinated Nb atom, referenced to $NbCl_6^-$). Mass spectrum data, niobium bearing fragments (m/e): 652 $[Nb_2O(OCH_2CH_3)_4(C_7H_5NO_2)_2]^+$, 607 $[Nb_2O(OCH_2CH_3)_3(C_7H_5NO_2)_2]^+$, 562 $[Nb_2O(OCH_2CH_3)_2(C_7H_5NO_2)_2]^+$, 547 $[Nb_2O(OCH_2CH_3)(OCH_2)(C_7H_5NO_2)_2]^+$, 517 $[Nb_2O(OCH_2CH_3)(C_7H_5NO_2)_2]^+$, 502 $[Nb_2O(OCH_2)(C_7H_5NO_2)_2]^+$, 489 $[Nb_2O(OH)(C_7H_5NO_2)_2]^+$. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O, and ^{93}Nb.

3.2. Crystal structure determination and refinement

A crystal of $0.20 \times 0.13 \times 0.10\ mm^3$ of **I** was removed from its liquor and mounted on a fiber glass. The diffraction measurements were conducted on a STOE IPDS-II diffractometer with graphite monochromated Mo Kα radiation, using the STOE X-AREA software package [21]. Cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of diffraction data from 6917 unique reflections for **I**. Data were collected at 298 K to a maximum 2θ value of 29.17° for **I** in a series of ω scans in 1° oscillations. Data were integrated using the Stoe X-AREA software package [21]. A numerical absorption correction was applied in each case using X-RED [22] and X-SHAPE [23] software. The structures were solved by methods and refined on F^2 using a full-matrix least-squares procedure with anisotropic displacement parameters [24]. Atomic factors were obtained from the International Tables for X-ray Crystallography (Kluwer Academic Publisher 1995). All refinements were performed using the X-STEP32 crystallographic software package [25]. Crystal data and refinement details are listed in Table 1. The highest peaks and deepest holes for this compound are around the Ta atom (a distance of 0.81 Å for highest peak and 0.77 Å for deepest hole).

An orange block shaped crystal of **II**, air stable at room temperature, was used for the crystallographic measurements and reported elsewhere [9].